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ADHESIVES FOR USE UNDERWATER

Richard W. Drisko, et al

Civil Engineering Laboratory (Navy)
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ADHESIVES FOR USE UNDERWATER, by Richard W. Drisko, J. B. Crilly, and R. M. Staples

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1. Adhesives 2. Bonding 3. Underwater heating I. ZF61-512-001-032

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INTRODUCTION

The Navy has many practical uses for an adhesive that can readily be applied to an underwater surface and will cure relatively rapidly, either by itself or with auxiliary heating, to form a strong bond. A few of the more common uses are:

(1) Attaching an explosive or surveillance package to enemy structures underwater

(2) Joining of structural components during underwater construction

(3) Attaching a fabricated structure to a foundation located underwater

(4) Attaching instrumentation or modifications to underwater structures

(5) Repairing damaged underwater structures

(6) Patching damaged underwater cables

(7) Encapsulating connections or other critical areas subject to deterioration underwater

(8) Salvaging or recovering equipment from the ocean floor

(9) Attaching and directing the explosive force of shaped charges used in underwater excavation and mining

The desired physical properties of the adhesive (e.g., curing time, bonding strength, etc.) would vary with the particular use, as well as with the temperature so that no one formulation would be best suited for all uses. In the investigation described in this report, the chief objectives were (1) to develop separate adhesive formulations that would cure rapidly in cold ($5^{o}C$) and in warm ($20^{o}C$) waters with good bonding strengths (i.e., 50 kg/sq cm or more), (2) to find or develop a system for easily mixing and dispensing the adhesive underwater, (3) to determine the storage life of such systems, and (4) to determine the feasibility of using heat to accelerate underwater curing of adhesives.

A recent report [1] describes a quick screening of three proprietary adhesives for use underwater, with special emphasis on rapid curing. Two of the products show promise.

BACKGROUND

Many systems, including a cofferdam concept [2], have been developed for the coating or repairing of steel structures between tides and underwater. The materials most commonly used to date for coating and patching steel underwater are viscous two-component epoxy systems called spash-zone compounds [3-7]. When used as an underwater coating, they are applied by hand to sandblasted steel at a thickness of 1/8 to 1/4 inch. When used as a potting or patching material, they are applied at much greater thicknesses. Their bonding strengths to sandblasted steel can approach 1,000 psi (about 70 kg/sq cm) or more [8]. Although they are easily handled by divers, they have two serious limitations in meeting the objectives of the investigation described in this report: (1) they are very slow reacting, requiring 1/2 day or more for curing, depending upon temperature, and (2) they cannot be used at temperatures below 15^{o}C (59^{o}F). For this reason the present investigation considered a two-component epoxy system with a much more reactive curing agent.

EXPERIMENTAL PROGRAM

Initial tests were conducted at 5^{o}C and 20^{o}C to determine if various epoxy resin and curing agent combinations would cure rapidly underwater at these temperatures to form a hard mass. It was found that many such combinations were available, but on further investigation it was found that they did not wet steel surfaces well. Thus, various natural and synthetic wetting agents were investigated to find one that would allow the mixed blend of epoxy and curing agent to wet a steel surface. Blown fish oil was found to be the best choice for this purpose. Similarly, by trial and error, a liquid mercaptan resin component was found to achieve a rapid cure. A test procedure was then developed to determine the bonding strength of various promising adhesive formulations applied to sandblasted steel under seawater.

Bonding Strength Test Procedure

The two-component parts of test epoxy adhesive formulations (100 grams total weight) were vigorously mixed in a paper cup with a steel spatula for 30 seconds. The mixed product was then smoothly and rapidly applied to a pair of sandblasted steel probes having a surface area of 1 sq cm. The coated probes were next positioned on a sandblasted steel plate at the bottom of a tray of seawater at the desired temperature. The test specimen was then removed from the water after a selected time, and the bonding strength of the adhesive to the plate was immediately determined on a table model Instron Testing Machine (Figure 1). The specimen (Figure 2) was pulled at a rate of 0.5 cm/min, and the breaking strength was measured on the recorder to the nearest 0.1 kg/sq cm.

Development of Formulations

Many preliminary formulations were investigated both at 5°C and 20°C in order to determine promising combinations of the many available epoxy resins, curing agents, wetting agents, pigments, fillers, and viscosity regulators to give the desired final product. Two of the most promising with which most of the later testing was done are shown in Table 1. The bonding strengths of the 20°C formulation at selected time intervals after application at 5°C and at 20°C are shown in Table 2. This formulation was very viscous and difficult to mix at 5°C. Thus, the 5°C formulation of Table 1 with a reduced viscosity was developed for use at this temperature.

An interesting modification of the 20°C formulation of Table 1 in which the cab-o-sil was omitted was developed for repairing damaged underwater electrical cables at Iceland. It was formulated for mixing aboard ship at about 20°C followed immediately by diver application under water at a temperature near freezing. Its underwater bonding strengths for curing at 5°C and 20°C are listed in Table 3.

Figure 3 shows how a damaged lead-sheathed electrical cable was patched at Iceland by filling in the area that had been abraded away and bonding on a patch of lead sheathing. Figure 4 shows the same cable cut in two to show how the repair was made.

Investigation of Kit for Mixing and Applying Adhesive Underwater

An investigation was conducted to find or develop a practical system for use by a diver in mixing and applying the underwater adhesive formulations of Table 1.

Initially a plastic envelope with a removable center divider was considered. Because of packaging and stability problems encountered with this system, a plastic cartridge of the type shown in Figure 5 was selected for further study. This cartridge has a metal foil divider which is secured in place with an outer fiberglass reinforced tape. To mix and apply the adhesive from the cartridge, the outer band of tape is removed and the plunger is rapidly pushed back and forth to mix the two components. The plunger rod is then removed and a nozzle is screwed in its place. Finally, the end cap is removed and the mixed adhesive is forced out the nozzle by pushing on the inner diaphragm with the plunger rod or with the thumb.

Laboratory test results (compare Tables 2 and 4) indicated that early bonding strengths were not as great when they were mixed in a cartridge as when mixed with a spatula in a cup. The greater bonding strengths with the latter mixing is probably related to a more thorough mixing. Bonding strengths of the cartridge-mixed 5°C formulation are given in Table 4.

A brief study was conducted to determine the storage life of the two formulations of Table 1 stored both at 5°C and at 20°C and both in the cartridge form of Figure 5 and in metal cans. Bonding strength tests run over a 15-month period of time indicated that when stored in cans, either at 5°C or at 20°C, the two formulations continued to retain good bonding characteristics well over 1 year. However, when stored in plastic cartridges, the bonding strengths declined markedly after 9 months.

A few simple experiments conducted with Navy divers indicated that the kits with adhesives packaged in the plastic cartridges shown in Figure 5 can be used very easily underwater.

Auxiliary Heating Studies

A brief study was conducted into accelerating the curing of adhesives underwater, especially in cold waters. A burst of high energy of short duration that would give the exothermic reaction of the epoxy system a push was desired rather than a lower level of heat spread over a longer period of time. A highly exothermic chemical reaction with water as one of the reactants appeared to be most promising. Black et al. [9] investigated methods of utilizing heat from the reaction of magnesium with water for military diver heating. Variations of this general reaction were investigated.

A number of variations in mixtures of magnesium, metal salts, acids, etc. (15 grams total weight) were added to seawater (250 ml) in a Dewar flask, and the changes in temperature were measured. A composition of powdered magnesium (3.4 grams), copper sulfate (1.3 grams) , and hydroxylamine hydrochloride (10.3 grams) was the most effective heating mixture of those tested and, consequently, was used in tests with the underwater adhesives.

The equipment used in the accelerated curing of adhesives underwater are shown in Figure 6. A sandblasted steel panel was placed in a tall petri dish (9.7 cm diameter and 4.6 cm high) containing 250 ml of seawater. Two steel probes were bonded, as previously described, to the panel using the 20°C formulation of Table 1 mixed with a spatula in a cup. Immediately after positioning of the probes, the powdered heating mixture (15 grams) was added, and a wooden cover was placed over the petri dish to minimize heat losses. The temperature rise was recorded and the specimen was tested after a predetermined period of curing. The temperature rise was usually 50°C to 65°C whether the test was conducted at 5°C or at 20°C. Summaries of the bonding strength results are given in Tables 5 and 6. It can be seen from these data that curing was much more rapid with than without heating. Final (24-hour) bonding strengths were about the same with or without heating at 20°C and with heating at 5°C, but were much less without heating at 5°C.

The chemical reactions which produced the heat in the above experiments also produced gases (hydrogen and ammonia) and considerable turbulence. No attempt was made to determine the actual chemical reactions involved or practical methods of containing the heat or venting the hydrogen gas when such a system might be used by a diver. The determination of the feasibility of such a system for underwater curing of adhesives was the sole objective of this study.

FINDINGS

1. An adhesive formulation was developed that could be mixed, applied, and cured underwater at 20°C.

2. Another adhesive formulation was developed that could be mixed, applied, and cured underwater at 5°C.

3. A cartridge system was found to be practical for mixing and extruding adhesives underwater.

4. Bonding strengths of adhesives mixed with a spatula had greater early bonding strengths than those mixed in the cartridge because of more complete mixing in the former system.

5. The underwater adhesive formulations could be stored in metal cans for 1 year or in plastic cartridges for 9 months without loss of bonding strength.

6. A simple chemical heating system was found to raise the temperature of 250 ml of water by 50°C to 65°C and to accelerate curing of epoxy adhesive formulations, particularly in cold (5°C) water.

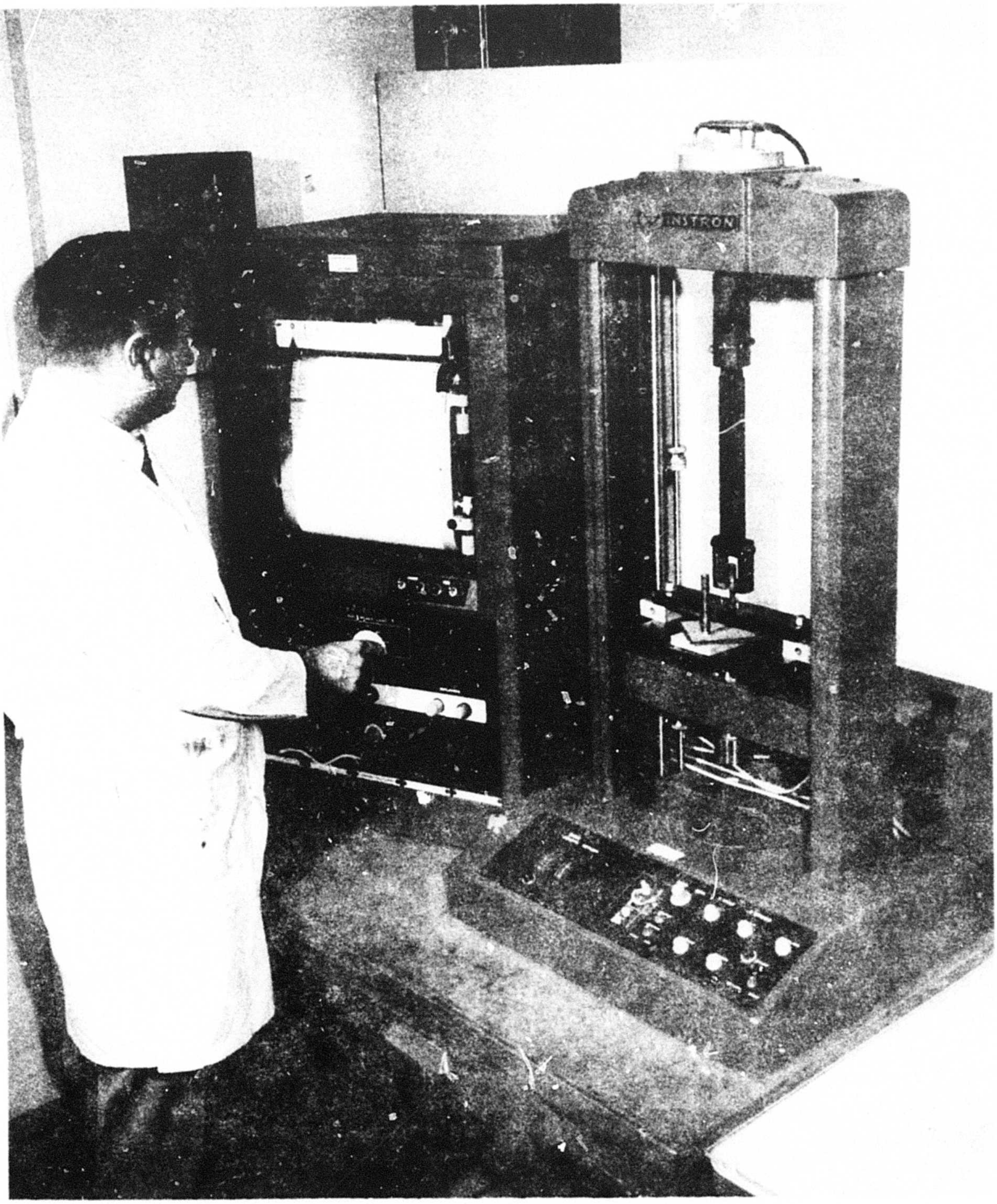

Figure 1. Table model Instron Testing Machine used in bonding strength tests.

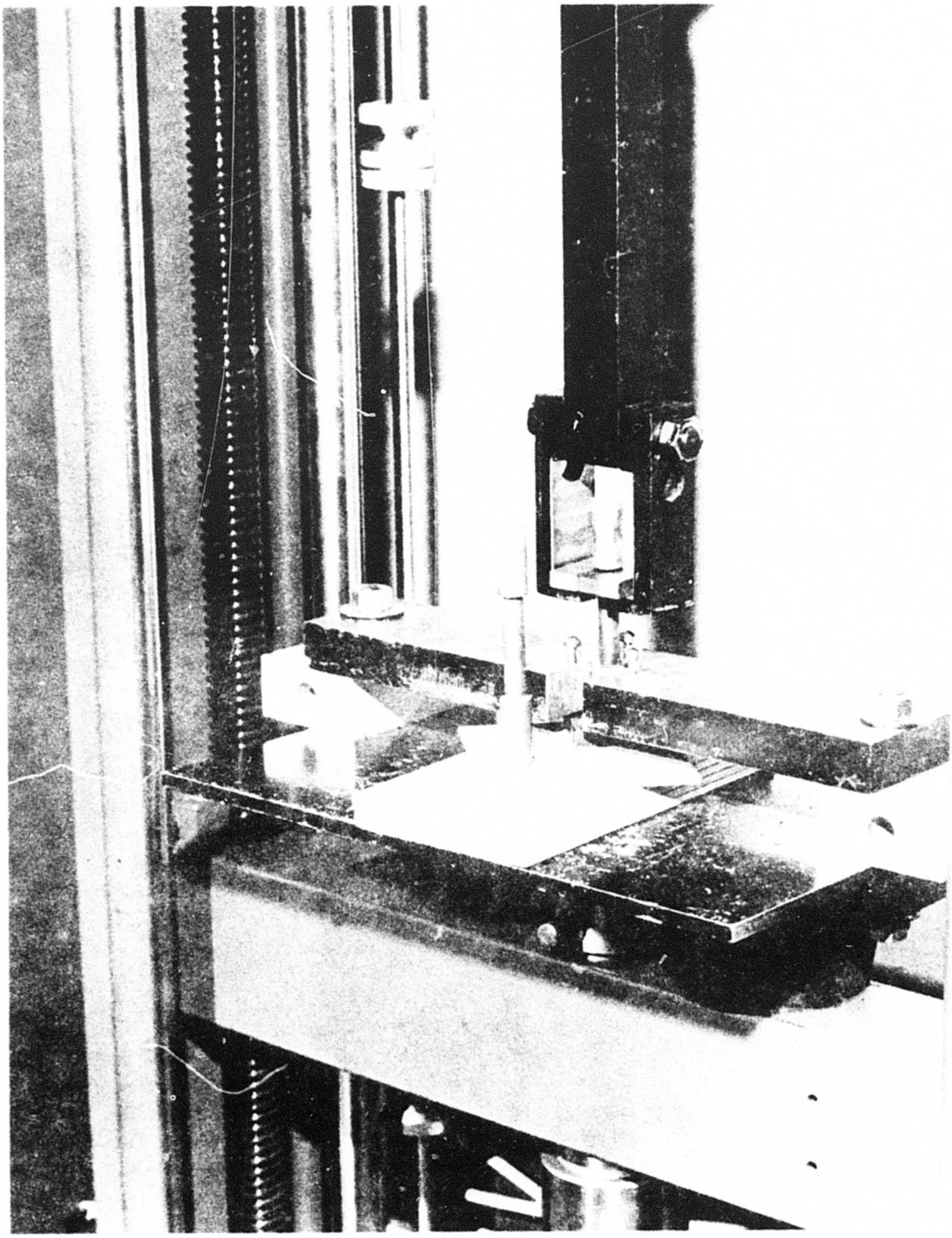

Figure 2. Bonding strength specimen in Instron Testing Machine.

Figure 3. Underwater electrical cable patched with adhesive.

Figure 4. Electrical cable cut in half to show patched area.

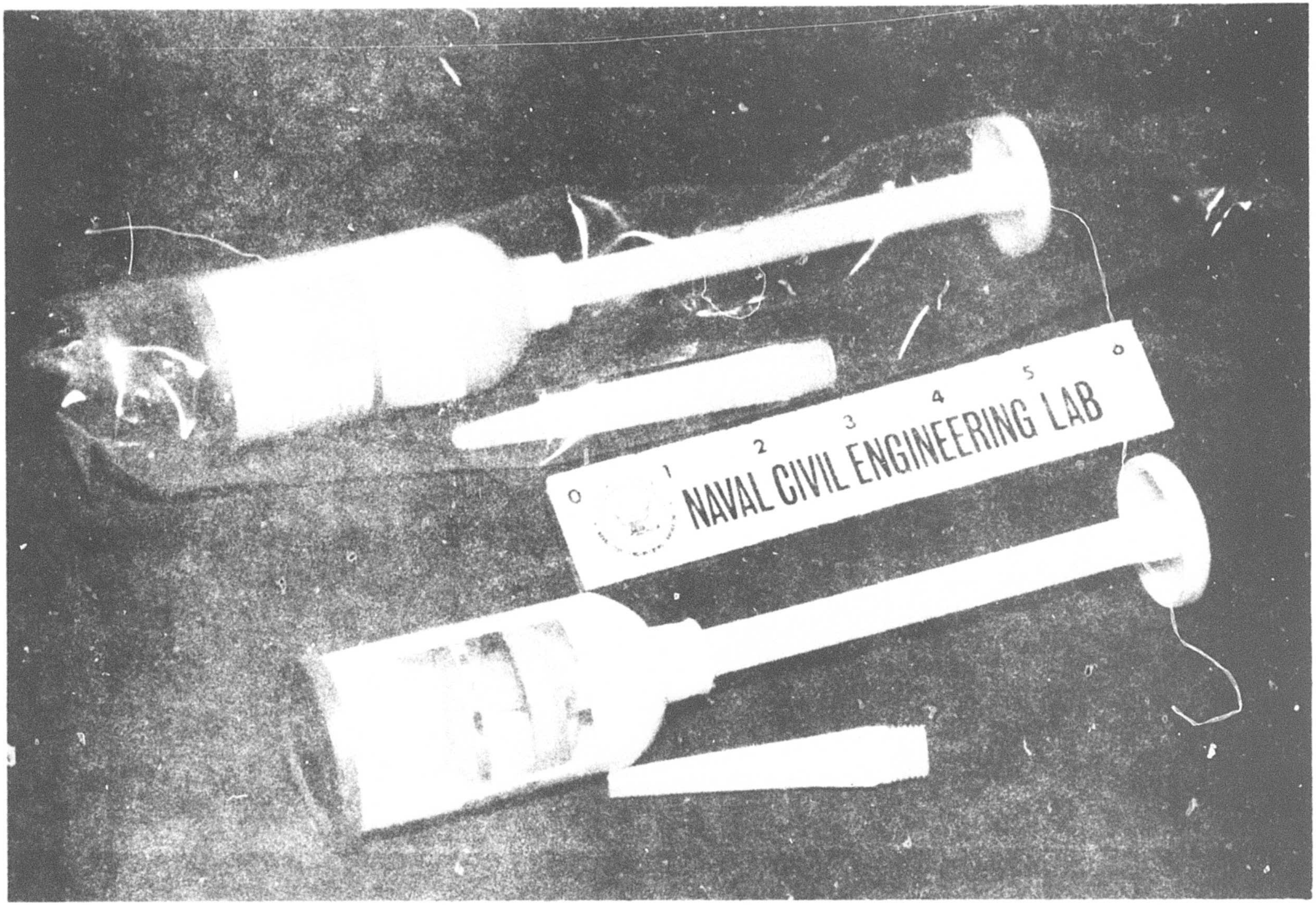

Figure 5. Plastic cartridges for underwater adhesive; upper in final packaged form, and lower cut away to expose interior.

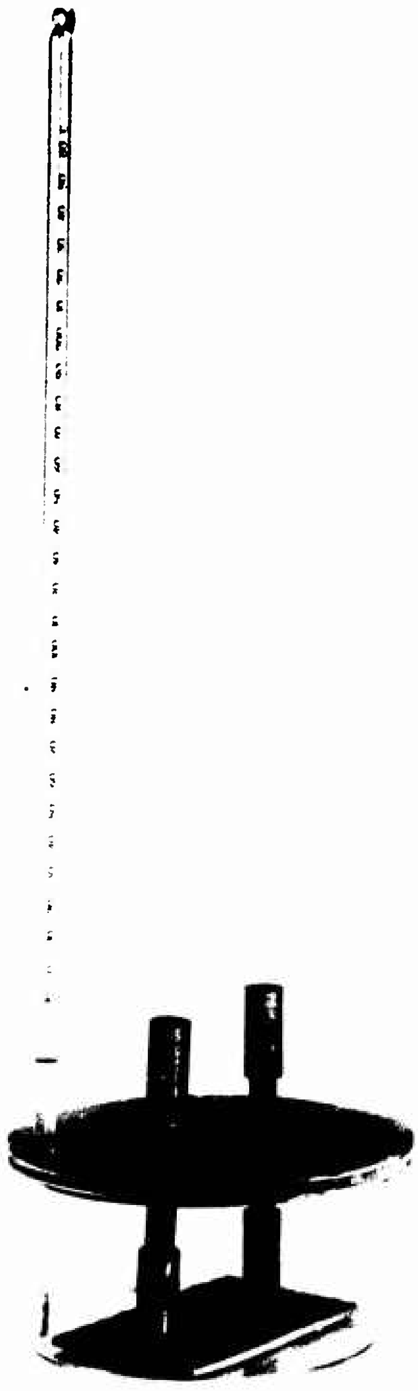

Figure 6. Equipment used in determining the effect of chemical heating on rate of curing.

Table 1. Formulations of Promising Underwater Adhesives*

Components	$20^{o}C$ Formulation (lb)	$5^{o}C$ Formulation (lb)
Part A		
Shell Epon 815 (epoxy resin)	-	78
Shell Epon 828 (epoxy resin)	100	8.7
Part B		
Diamond Shamrock DPM 3-800LC (polymercaptan)	100	100
Pacific Vegetable Oil Blown Fish Oil Z-7-1/2	20	20
2,4,6-Tri(dimethylamino-methyl) phenol	10	10
Cabot cab-o-sil M-5	5	-
Carbon Black	0.01	0.005
Cardura E (viscosity reducer)	-	10

* While sources of the raw materials are listed for complete identification, equivalent materials from other sources may be used.

Table 2. Bonding Strengths of the Hand-Mixed 20°C Formulaticn of Table 1

Curing Time (hr)	Bonding Strength (kg/sq cm)*-	
	Applied at 20°C**	Applied at 5°C
1/2	19.6	2.7; 1.6
2	42.8	10.5; 8.0
6	57.2	59.0; 26.0
24	56.8	60.0; 38.5

* Multiply the figures by 14.2 to convert from kg/sq cm to psi.
** Average of five--eight samples prepared at different times.

Table 3. Bonding Strengths of Iceland Formulation

Curing Time (hr)	Bonding Strength (kg/sq cm)-	
	Applied at 20°C	Applied at 5°C
1/2	18.3; 44.5	9.4; 5.4
2	28.0; 25.5	17.4; 25.5
6	39.0; 33.0	28.8; 36.3
24	50.0; 46.0	77.0; 38.0

Table 4. Bonding Strengths of Cartridge--Mixed Formulation

Curing Time (hr)	Bonding Strength (kg/sq cm)-	
	20°C Cure	5°C Cure
20°C Formulation		
1/2	12.3; 11.1	uncured
2	19.5; 19.5	4.0; 5.5
6	30.0; 31.0	10.0; 8.0
24	44.0; 57.5	16.5; 9.5
5°C Formulation		
1/2	18.4; 22.8	5.6; 4.2
2	45.5; 64.5	20.3; 8.5
6	102.0; 52.0	57.0; 33.5
24	58.5; 53.0	47.0; 34.0

Table 5. Bonding Strength of 20°C Formulation With and Without Auxiliary Heating at 20°C

Curing Time (hr)	With Heating		Without Heating	
	Number of Specimens	Average Bonding Strength (kg/sq cm)	Number of Specimens	Average Bonding Strength (kg/sq cm)
1/6	2	20.7	2	1.3
1/2	8	34.6	10	19.6
2	8	52.9	10	42.8
6	5	49.7	9	57.2
24	6	50.6	10	56.8

Table 6. Bonding Strengths of 20°C Formulation With and Without Auxiliary Heating at 5°C

Curing Time (hr)	With Heating		Without Heating	
	Number of Specimens	Average Bonding Strength (kg/sq cm)	Number of Specimens	Average Bonding Strength (kg/sq cm)
1/6	2	13.0	2	0*
1/2	7	17.9	8	2.1
2	8	28.1	8	21.1
6	8	35.9	8	27.9
24	8	51.0	6	33.9

* Unbonded.

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